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THE USE OF INHIBITORS TO REDUCE THE CORROSION OF AUTOMOTIVE STEELS IN A CHLORIDE ENVIRONMENT

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DECEMBER 1981

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REPORT MRP/PMRL 81-80(TR)

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THE USE OF INHIBITORS TO REDUCE THE CORROSION OF AUTOMOTIVE STEELS IN A CHLORIDE ENVIRONMENT

by

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ABSTRACT

The effects of inhibitors on corrosion, in terms of weight loss, were compared by an intermittent immersion test method. The inhibitors were sprayed intermittently on corroding steel coupons.

All but one of the inhibitors showed beneficial effects. A polyphosphate inhibitor was the best of those tested and was also the most convenient to use.

To further this work it would be advisable to field test inhibitors under controlled conditions on one or more automobiles using similar automobiles as controls.

INTRODUCTION

A 28-day intermittent immersion test conducted on uncoated automotive steels, in the laboratory, provided a ranking of the steels similar to that obtained by under-car testing (1). The mode of corrosive attack under laboratory conditions was similar to that observed in the creviced region of under-car specimens and in sections of automotive panels corroded in service.

The corrosion rates, per annum, for the 28-day laboratory test were 11 to 16 times greater than those shown per annum by six months of under-car testing during a continuous winter-spring season in the Ottawa region. This increased rate of corrosion combined with the similar ranking of materials tested by both methods, indicated that the laboratory test provided a suitable and fast means of ranking automotive steels exposed to de-icing salts.

A study of the effects of inhibitors believed to be environmentally innocuous was undertaken to determine their potential value in reducing corrosive attack when sprayed intermittently on steel surfaces (2). If effective, a spraying schedule for automobiles could be adopted to reduce rates of corrosion attributed to the use of de-icing salts on roadways. The laboratory test method was adapted for this purpose and tests were undertaken to determine the effects of several inhibitors.

MATERIALS

A commercial quality cold rolled (CQCR) sheet steel typical of carbon steel used in automobiles was used for these tests. Its chemical composition is shown in Table 1.

EXPERIMENTAL PROCEDURES

General

Previous laboratory tests involved the intermittent immersion of steel specimens into a 3.5% solution of sodium chloride in water (1). The specimens were coupons approximately 0.075 cm thick and 3.8 cm square. They were assembled in groups of five and suspended on a plastic rod as shown for arrangement No. 2 in Fig. 1. Small non-conducting plastic spacers 0.15 cm thick provided the desired crevice spacing between coupons. In this configuration the three control coupons experience identical crevice environments while the two end coupons of the assembly are exposed on one free surface.

The intermittent immersion equipment used previously was redesigned to permit testing inhibitors (1). The components shown in Fig. 2 are:

1. storage vessel to provide a continuous supply of 3.5% Na Cl solution;
2. two vessels - the inner contained the Na Cl solution in use and the outer provided a water jacket for temperature control;
3. two vessels - the inner contained the specimens tested with inhibitors and the outer was a water jacket interconnected with other jackets;
4. two vessels - as in 3 except that the inner vessel contained control coupons not subjected to inhibitors.

Additional vessels located behind 3 and 4 contained supplies of the inhibitors.

The remaining equipment consisted of timers, pumps, valves and portable temperature controlling units.

A pump and valve arrangement maintained the required level of the corrosive solution in use in vessel 2. The corrosive solution from inner vessel No. 2 was pumped separately from the common source into the two small vessels containing the specimens using a timed cycle. The used solution was discarded through solenoid valves linked to the timing cycle after the specimens had been immersed for a predetermined time. A separate pump completed the timed cycle by spraying inhibitor for 15 s every 12 h over the group of specimens in one of the vessels. The spray was applied at a rate of 200 mL/min through a garden hose nozzle located above the specimens. The specimens in vessel No. 4 were not sprayed with inhibitor as they were used as controls.

The 12 h interval used for the inhibitor application was selected to represent a weekly interval in terms of the differential rates of corrosion between laboratory and under-car testing.

Specimen Preparation

The specimens were prepared by a light grit blasting (-150 mesh), degreasing in trichlorethylene and weighing (1). Following exposure to corrosive attack the specimens were derusted and reweighed. Derusting was accomplished by scrubbing the coupons under running water and immersing them for 15 min at ambient temperature in a 50% solution of concentrated HCl in distilled water. The addition of 1 mL of corrosion inhibitor Rodine 213 to the derusting solution prevented any significant attack on the coupons during the derusting period.

Environment

It was demonstrated during the development of the intermittent immersion technique that results of corrosion within the crevices in terms of weight loss after 14 to 28 day test periods did not differ appreciably between temperatures of 20° and 30°C, and between relative humidities (RH) of 30% and 80% (3). Consequently, no control was exercised over humidity. However, the corrosive chloride medium was maintained at approximately 20°C by circulation of the water through the water-jackets during the testing period.

Although distilled water was used for the NaCl solution in the previous tests (1), tap water was used throughout for these preliminary inhibitor tests because a large quantity of solution was required.

Inhibitors

The inhibitors used in these tests will be identified as follows:

A. Proprietary polyphosphate containing additives (calcium, zinc, and nitrites).

B. Commercial polyphosphate with calcium subsequently added to the commercial mix to improve its inhibition (4).

C. Sodium molybdate.

D. Commercial polyphosphate as in B plus an organic inhibitor, ethoduomeen, T13, applied sequentially (2).

Tests

Test No. 1 - Inhibitor A

Inhibitor A was used in solution. However, this commercial inhibitor was designed for use as a solid mixed with de-icing salt and, when added in the proportion of 25% by weight to tap water, produced a bulky orange/yellow precipitate. The liquid phase of the saturated solution was decanted and used for this test. An analysis of the decanted solution showed levels of 92.2 g/L phosphorus, 7.8 g/L zinc and 41.4 g/L calcium. It was determined from these values that the solubility of the solid inhibitor in tap water was approximately 6% by weight based on the saturation by zinc and phosphorus*.

The cycle was timed to provide 3 min immersion followed by 20 min of drying.

Test No. 2 - Inhibitor B

Inhibitor B was completely soluble at 25% by weight in tap water. However, the addition of $CaCl_2$ to this solution at ambient temperatures caused the formation of a white precipitate. The decanted solution was used for this test. The composition of the decanted solution was 35.6 g/L phosphorus and 6.1 g/L calcium ion. Therefore, based on 90.2 g/L phosphorus in the original 25% solution before precipitation, it was calculated that the decanted solution represented a 9.9% solution of polyphosphate which was saturated by 6.1 g/L of calcium ion.

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*If a 6% solution, by weight, of A is used instead of the decanted liquid from the 25% solution the quantities of Zn and P in solution would remain as above, but the quantity of Ca would be reduced about 4 times or in proportion to the reduction in the quantity of the inhibitor.

In addition to adding $CaCl_2$ to the inhibitor solution, 0.5% $CaCl_2$ by weight was added to the 3.5% chloride solution to ensure the presence of calcium for the inhibitor reaction.

The cycle was timed to provide 3 min immersion followed by 20 min of drying.

Test No. 3 - Inhibitor B

Inhibitor B was again used in Test No. 3. It was mixed to give approximately the same concentration as the decanted solution used in Test No. 2. This was accomplished by mixing 10 per cent by weight of sodium polyphosphate (calgon) in tap water and adding 16.9 g/L of $CaCl_2$ to provide 6 g/L of calcium ions.

Calcium chloride was not added to the corrosive solution of 3.5% NaCl, in this test.

A cycle of 3 min immersion followed by 2 h of drying was used instead of 20 min of drying as in Test Nos. 1 and 2.

Test No. 4 - Inhibitor C

All the conditions of Test No. 4 were identical to those for Test No. 3 but sodium molybdate at a concentration of 250 mg/L was used as the inhibitor.

Test No. 5 - Inhibitor D

A combination of polyphosphate inhibitor B with the organic inhibitor ethoduomeen, T13, was used for this test. The concentrations of the two inhibitors were 10% polyphosphate by weight with 6 g/L of calcium ions and 5% ethoduomeen by weight. The inhibitors were applied in sequence for 15 s each at 12 h intervals. The polyphosphate was applied first.

The cycle was 3 min immersion and 2 h of drying as in Tests 3 and 4.

RESULTS AND DISCUSSION

Test No. 1 - Inhibitor A

The results in terms of weight loss for the first complete 28 day test using an inhibitor spray are given in Table 2.

The results show that the weight loss of the "inhibited" group of coupons was substantially reduced when compared with the weight loss of the uninhibited control group of coupons. However, some difficulties were encountered with leakage during this test that caused inconsistencies in the timing cycle and possibly some effect on the weight loss.

Although the test was designed to provide data from the three inner specimens only, an average of the weight loss of the two outer coupons was also calculated for comparison. A slightly higher rate of corrosion has frequently been observed on outer coupons in the absence of an inhibitor. Inhibition is defined as the difference in weight losses between uninhibited and inhibited specimens as a percentage of the weight losses for the uninhibited specimens.

A limited evaluation of pitting severity in terms of average pit depths indicated that inhibition reduced pitting severity by a factor of approximately two.

Test No. 2 - Inhibitor B

This test was completed without difficulty after some modifications were made in the equipment. The results are shown in Table 3.

The use of the inhibitor in this test reduced the average weight loss by a factor of approximately five or 80% inhibition for both the three inner and the two outer coupons.

Test No. 3 - Inhibitor B

Inhibitor B was used for this test with the modifications described under 'tests'. The results are shown in Table 4.

The inhibition was approximately 74% for the inner coupons and 82% for the outer ones.

A comparison of the "uninhibited" controls for Test Nos. 2 and 3 shows a similar average weight loss for the three inner coupons. However, the outer two coupons show a greater loss in Test No. 3. This indicates that the longer 2 h drying period does not greatly alter the corrosion rate of the three inner coupons.

The weight losses of the "inhibited" group in Test Nos. 2 and 3 do not differ appreciably. However, both show lower weight losses than the "inhibited" group in Test No. 1. Furthermore, the control group in Test No. 1

shows a greater weight loss than the control group in either Test No. 2 or No. 3. These observations indicate that some loss of control in Test No. 1 prevents direct comparison with subsequent tests, although benefits from the inhibitor are apparent.

Test No. 4 (Inhibitor C)

The results of using a solution of 250 mg/L of molybdate compared with using no inhibitor are given in Table 5. These results are based on only one test and one concentration and show no benefits from the use of this inhibitor.

Test No. 5 (Inhibitor combination D)

The results obtained using this combination of inorganic and organic inhibitors are shown in Table 6. These results show approximately 70% inhibition.

The results of this single test compared with those shown in Tables 2 and 3 indicate no advantage in combining the two inhibitors. However, other untried cyclic combinations might show benefits not evident here.

GENERAL DISCUSSION

These tests are a first attempt to evaluate the potential of spraying inhibitors on motor vehicles to reduce the corrosive effects of de-icing salts. Although conditions and timing schedules were estimated and based on a possible routine application at weekly intervals during the winter season, substantial benefits were indicated in terms of reduced weight losses for all the inhibitors except the molybdate solution. These benefits, as summarized in Table 7, vary from about 70 to 80% inhibition.

The simplest inhibitor to use, type B, gave good results that are not directly comparable with those of type A, test No. 1. Because inhibitor A is not convenient to use in solution, and inhibitor D is more complex to use because of its dual requirement, these tests suggest a strong preference for type B.

CONCLUSIONS

Inhibitors applied periodically by spraying show promise of substantially reducing corrosive attack by de-icing salts on automobiles.

REFERENCES

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4. Uhlig, H.H., Triadis, D.N. and Stern, M., "Effects of Oxygen, Chlorides, and Calcium Ion on Corrosion Inhibition of Iron by Polyphosphates", Journal of the Electrochemical Society, vol. 102, no. 2; Feb 1955.

Table 1. Composition* of the commercial quality cold rolled steel sheet.

Per Cent

C	Mn	Si	S	P	Sn	Ni	Cr	Mo	V	Al	Cu
0.08	0.33	<0.003	0.015	<0.002	0.007	0.01	0.05	<0.01	<0.005	<0.005	0.0

*Quantometer spectrochemical analysis.

Table 2. Weight loss comparison between "inhibited" and "uninhibited" corroded specimens using inhibitor A.

Test No. 1

	Uninhibited	Inhibited
Specimens	Weight loss mg/cm^2	Weight loss mg/cm^2
1 outer	74.4	13.7
2 inner	67.3	13.9
3 inner	57.7	14.4
4 inner	61.1	12.7
5 outer	70.6	10.6
Av. (inner)	62.0	13.7
Av. (outer)	72.5	12.2

Inhibition 3 inner coupons ~ 78%*

Inhibition 2 outer coupons ~ 83%

$$* = \frac{\text{wt loss uninhibited - wt loss inhibited}}{\text{wt loss uninhibited}} \times 100$$

Table 3. Weight loss comparison between "inhibited" and "uninhibited" corroded specimens using inhibitor B.

Test No. 2

	Uninhibited	Inhibited
Specimens	Weight loss mg/cm^2	Weight loss mg/cm^2
1	37.2	7.0
2	32.9	6.9
3	33.3	6.8
4	33.6	6.8
5	33.8	6.6
Av. (inner)	33.3	6.9
Av. (outer)	35.5	6.8
	Inhibition 3 inner coupons ~ 80%	
	Inhibition 2 outer coupons ~ 80%	

Table 4. Weight loss comparison between inhibited and uninhibited corroded specimens using inhibitor B.

Test No. 3*

	"Uninhibited"	"Inhibited"
Specimens	Weight loss mg/cm^2	Weight loss mg/cm^2
1	47.2	10.6
2	29.9	10.8
3	32.0	9.1
4	40.0	7.2
5	50.8	6.7
Av. (inner 3)	33.9	9.1
Av. (outer 2)	35.5	6.8
	Inhibition 3 inner coupons ~ 74%	
	Inhibition 2 outer coupons ~ 82%	

*Test No. 3 differed from test No. 2 in two aspects: (1) A 2 h drying period instead of 20 m; (2) $CaCl_2$ was added to inhibitor only and not to the corrosive solution.

Table 5. Weight loss comparison between "inhibited" and "uninhibited" corroded specimens using inhibitor C.

Test No. 4*

	Uninhibited	Inhibited
Specimens	Weight loss mg/cm^2	Weight loss mg/cm^2
1	37.7	35.7
2	32.7	30.7
3	28.2	30.7
4	30.2	29.9
5	41.1	31.2
Av. (inner)	30.4	30.4
Av. (outer)	39.4	33.5
	No apparent inhibition.	

*Test parameters the same as for test No. 3.

Table 6. Weight loss comparison between "inhibited" and "uninhibited" corroded specimens using inhibitor combination D.

Test No. 5*

	Uninhibited	Inhibited
Specimens	Weight loss mg/cm^2	Weight loss mg/cm^2
1	31.4	9.1
2	21.0	6.2
3	22.1	7.0
4	23.8	7.9
5	33.0	10.3
Av. (inner)	22.3	7.0
Av. (outer)	32.2	9.7
	Inhibition 3 inner coupons ~ 69%.	
	Inhibition 2 outer coupons ~ 70%.	

*Test cycle the same as for test No. 3.

Table 7. Summary of results for inhibitors used in these tests.

Inhibitors	Inhibition per cent*
A	78
B (test 2)	80
B (test 3)	74
C	0
D	69

*Inner specimens only

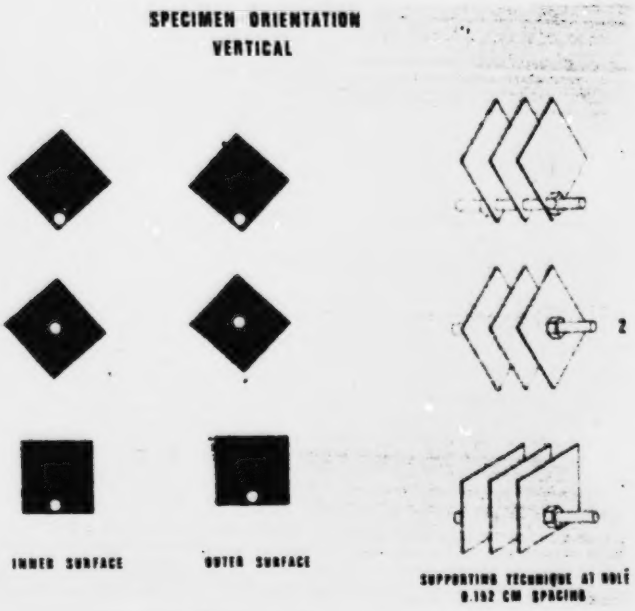

Fig. 1. Some examples of specimen orientation from which the No. 2 arrangement was selected (1). (neg 1494)

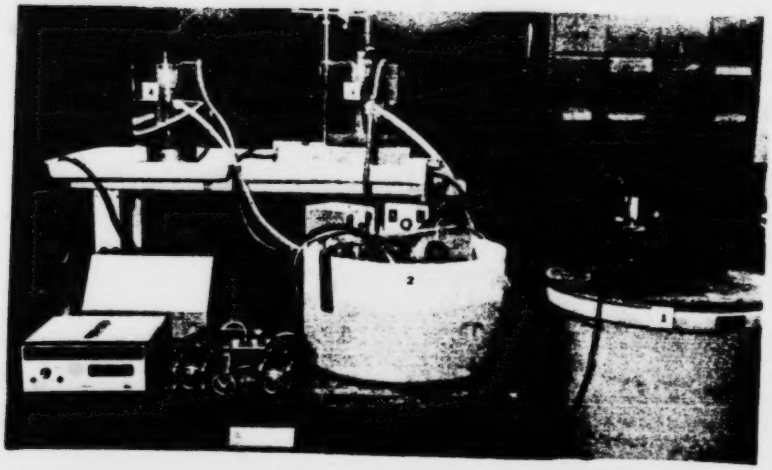

Fig. 2. Apparatus used for experimental intermittent immersion tests in 3.5% NaCl with inhibitor spray. (neg 3933)